MACCCR Third Annual Fuels Summit

Chemistry and Transport Properties for Jet Fuel Combustion

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Role of diffusion

Ignition characteristics of n-C_7H_{16}[1]

- 10% perturbation of diffusivity

  → 50K change of ignition temperature
- Sensitivity of ignition to diffusion ≈ sensitivity to kinetics

Extinction of CH_4/air flame[2]

- Analysis with average and multiple diffusion models

  → 20 ~ 40% discrepancies in extinction strain rate

[1] M. G. Andac et. al., *31th Int. Sym. Combust., 2007, pp. 1165*

[2] H. Wang et. al., *Combust. and flame, 2005, Vol 142, pp. 374*

Approaches to determine diffusion properties

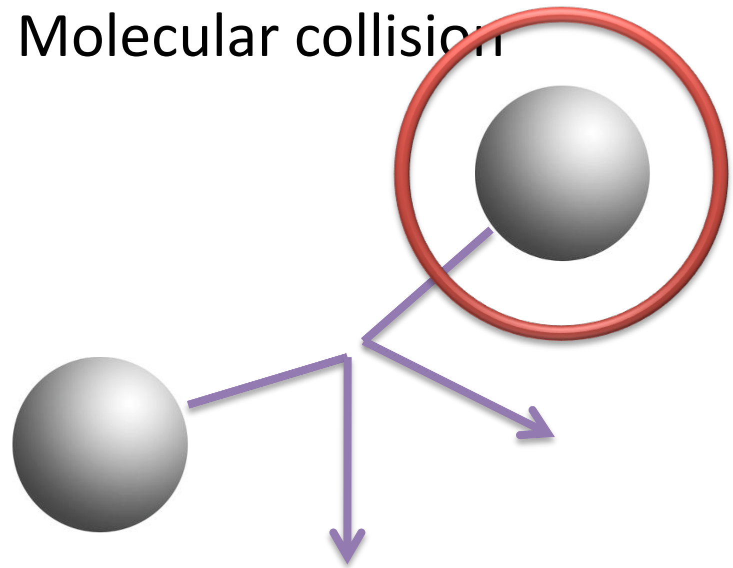
Experiment
Very little

Gas Chromatographic (GC)

Theory

Gas Kinetic Theory (GKT)

Molecular collision



Spherical molecules

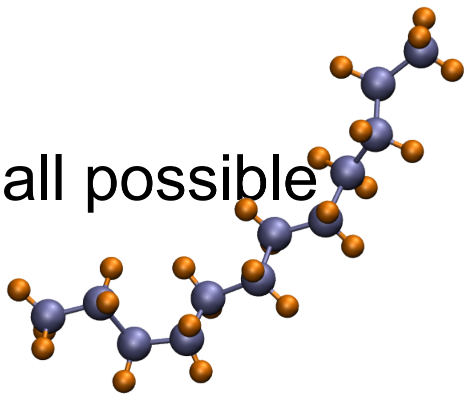
Simple analytical equation

$$D_{12} = \frac{3}{8}\frac{\sqrt{(k_B T)^3/(2\pi m_{12})}}{n\sigma_{12}^2 \langle \Omega^{(1,1)*} \rangle}$$

Polyatomic Molecules

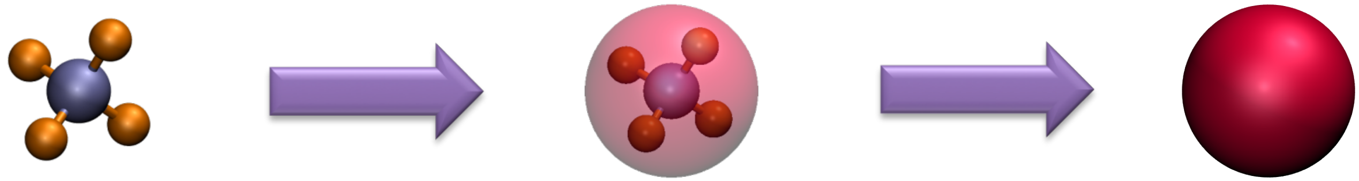
Dynamics of Molecular Collisions

- Have internal degrees of freedom. Collision can involve change in rotation and vibration energies.
- Interact through non-spherical intermolecular pair potential energies.
- Internal degrees of freedom for transporting energy – in GKT/C-E only binary elastic collisions are considered without internal degrees of freedom
- Collision integrals must be averaged over all possible relative orientations occurring in collision.

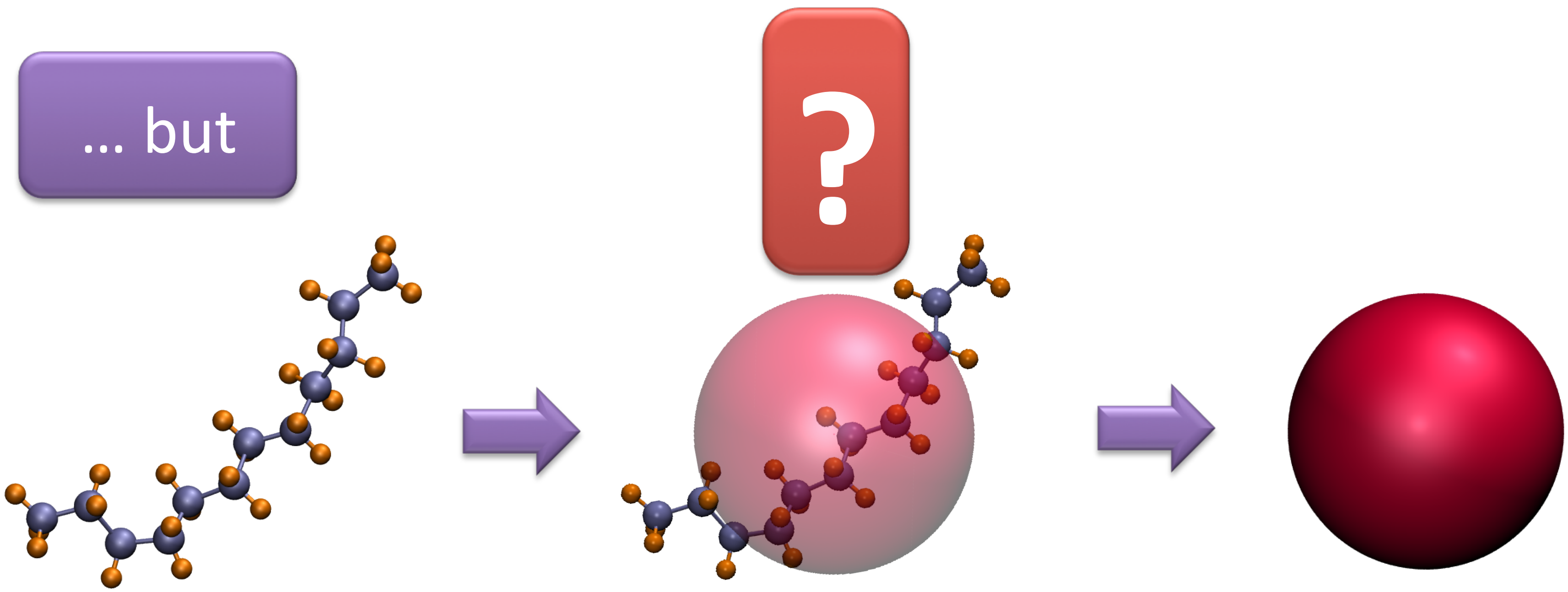


Validity of GKT

Simple…

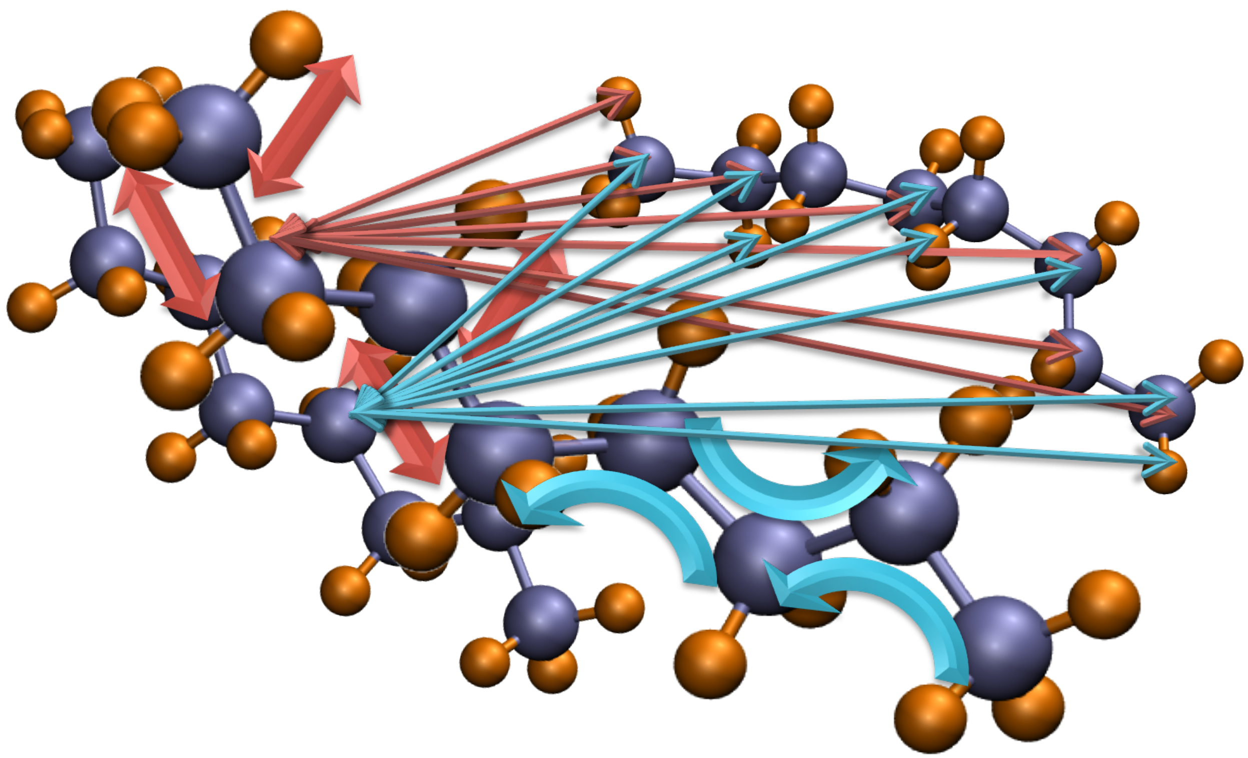


… but



How to include molecular structures?

MD & all-atom potentials



Green-Kubo formula

Thermodynamic factor

Auto correlation

Cross correlation

$$D_{12} = Q\left[x_2 D_1 + x_1 D_2 + x_1 x_2 \left(\frac{f_{11}}{x_1^2} + \frac{f_{22}}{x_2^2} - 2\frac{f_{12}}{x_1 x_2}\right)\right]$$

Mole fraction

D as ensemble average of velocity functions

$$D_\alpha = \frac{1}{3}\int_0^\infty \left\langle \vec{u}_i^{\alpha}(t)\cdot \vec{u}_i^{\alpha}(t+\Delta t)\right\rangle dt \qquad f_{\alpha\beta} = \frac{1}{3}\int_0^\infty \left\langle \vec{u}^{\alpha}(t)\cdot \vec{u}^{\beta}(t+\Delta t)\right\rangle dt$$

Computational details

Canonical ensemble (NVT)

- Global thermostat

300 alkanes + 3000 nitrogens

- 500 ~ 1000K, 1 atm

Molecules as fully flexible - bond stretching, angle vibration, and change of torsion angle.

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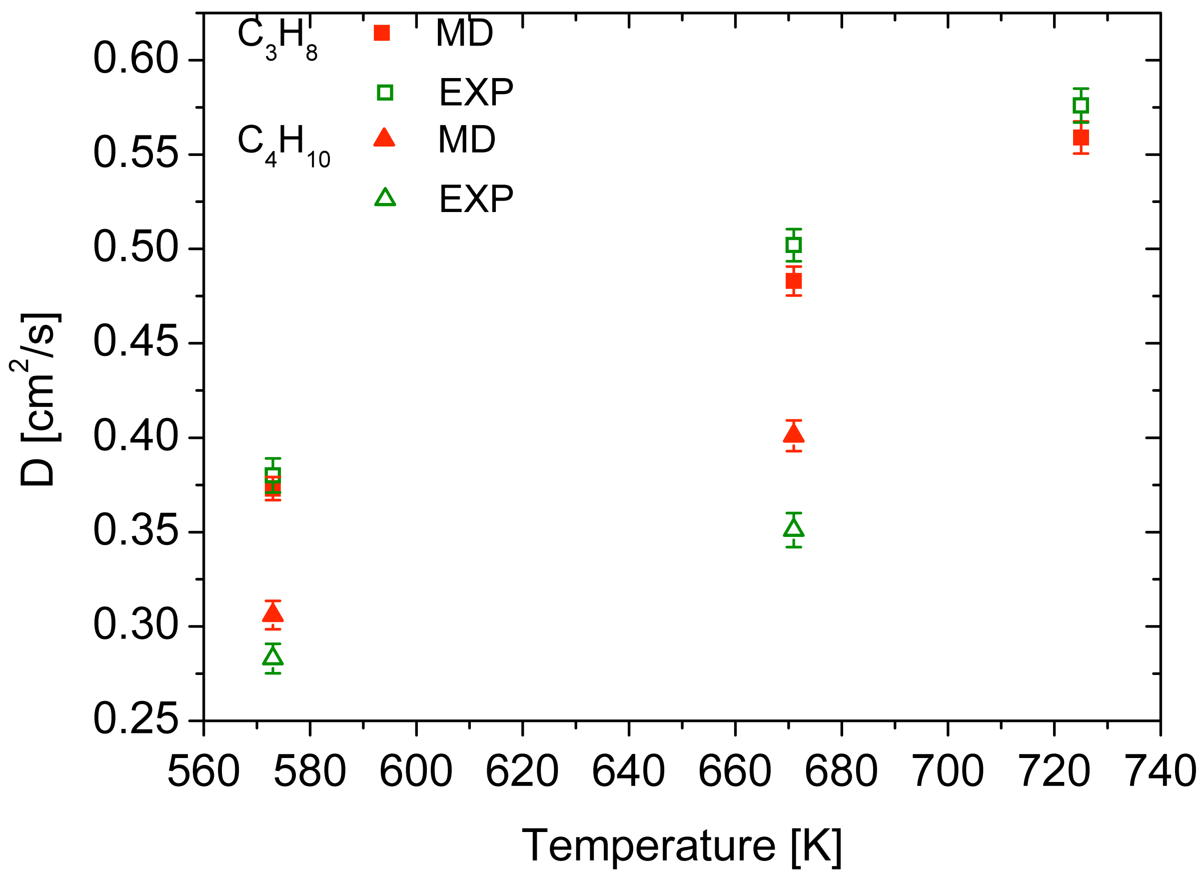
Benchmark

Comparison with available experimental data[1,2]



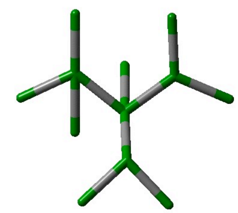
Good agreement with EXP.

[1] A. Manion et. al., *Combustion inst. tech. meeting, 2008*

[2] W. A. Wakeham et. al., J. Phys B, *1973, Vol 6, pp. 886*

N-dodecane

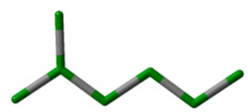
D_{12} [cm^2/s]



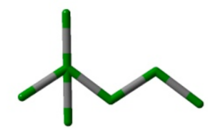
T(K)	MD – d1	C-E	MD – d2
500	**0.1105**	**0.1351**	**0.1267**
1000	0.3913	**0.4705**	**0.4355**
1500	**0.8021**	**0.9446**	**0.9027**

Heptane isomers

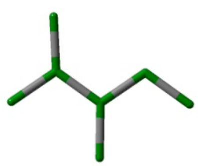
n-C_7H_{16}
normal heptane



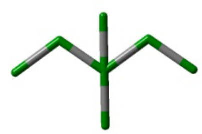
2-C_7H_{16}
2-methylhexane



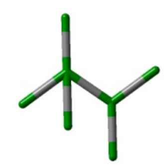
2,2-C_7H_{16}
2,2-dimethylpentane



2,3-C_7H_{16}
2,3-dimethylpentane



3,3-C_7H_{16}
3,3-dimethylpentane



2,2,3-C_7H_{16}
2,2,3-trimethylbutane

Chae, Violi, J. Chemical Physics, in press

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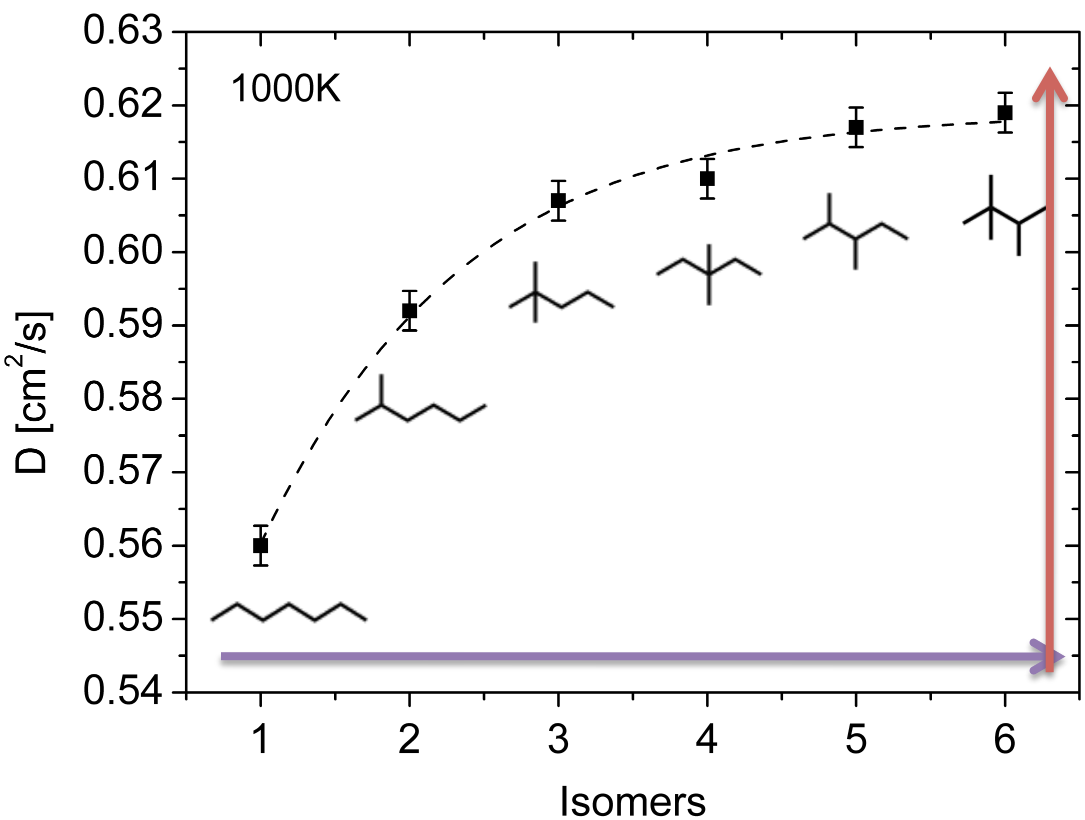
Diffusion coefficients



D ↑

# of methyl branches ↑

Effect on flame

MD
- Detailed structures
- For all molecules

GKT
- Sphere
- For small molecules

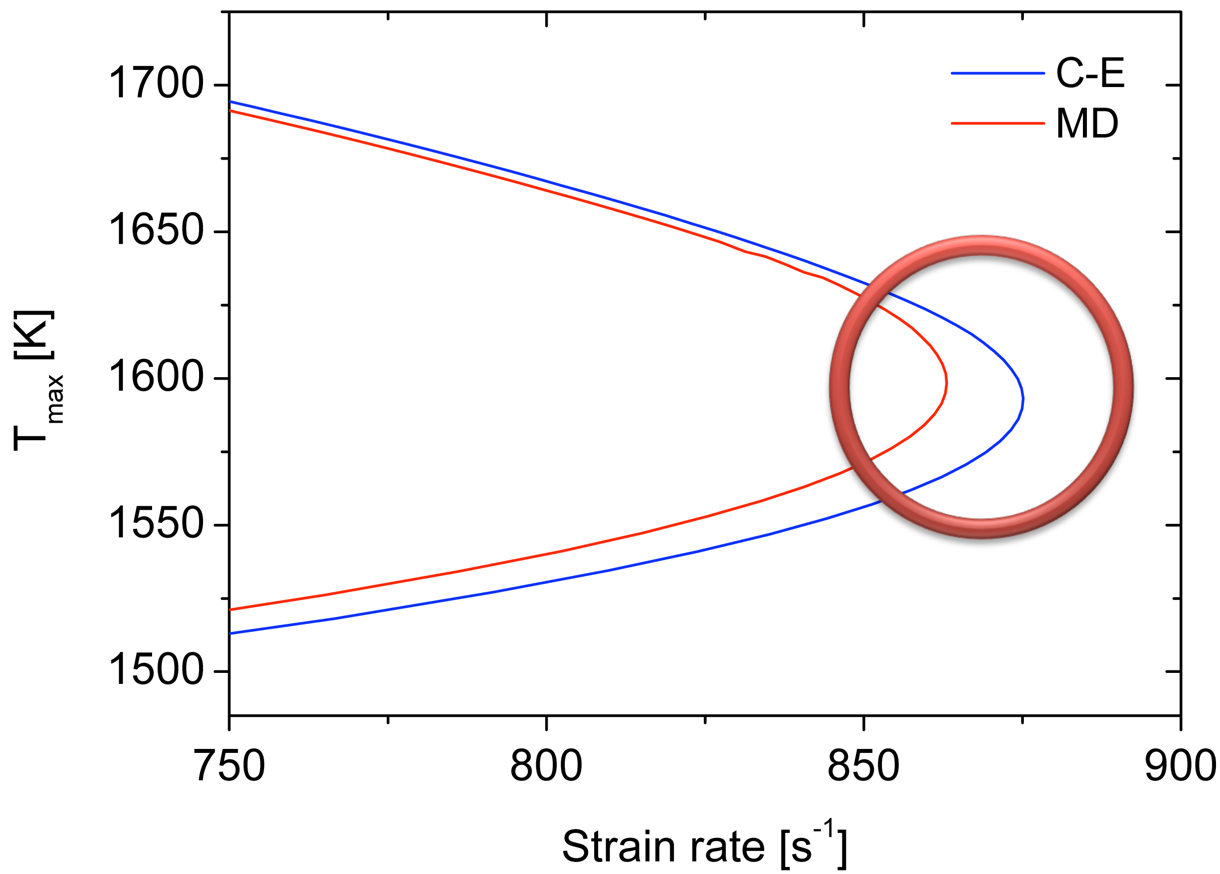
Important in flame?

Test the effect of diffusion on flame

- Non premixed $C_{12}H_{26}$ flame
- Opposed jet burner
- Compare extinction point

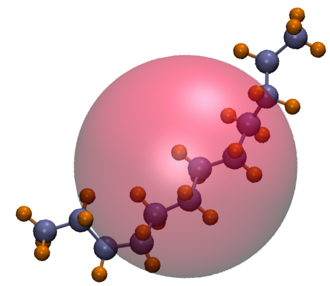
Extinction

$C_{12}H_{26}$ non-premixed opposed jet flame

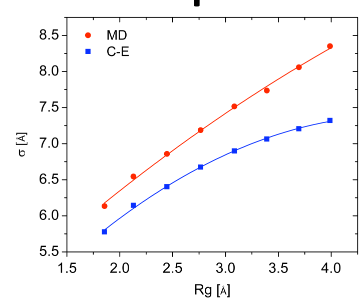


Conclusions

- Gas kinetic theory (GKT) becomes inaccurate as non-sphericity of a molecule increases.



- The root of the error in GKT is the assumption of spherical structures for particles.



- MD can quantify the effect of molecular structures and provide correction factors for GKT (Rg) .